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Background Concentration of Sulfate in
Precipitation along the West Coast of North America

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along the West Coast of North America**

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ABSTRACT

The pH is not sufficient to characterize the acidity of precipitation, but rather its acid-base components must be described. The chemistry of natural emission sources as well as the mechanisms of precipitation formation are key factors in determining the chemistry of precipitation along the west coast of North America. With the ocean biota as a source of atmospheric aerosol sulfate, it is expected that this "background" chemistry will be dominated by sulfate. For the purpose of this study, background was defined as a remote site generally upwind of urban areas, with the additional requirement that data with evidence of contamination by anthropogenic sources be excluded. Data from long term precipitation monitoring sites along the coasts of Oregon, Washington, and British Columbia were evaluated to estimate a background sulfate concentration in precipitation. In addition to screening the data for charge balance, collection efficiency, and anthropogenic influence, the data were corrected for sulfate associated with sea salt. The results of this analysis suggest that background excess sulfate concentration in rainfall along the West Coast of North America occurs most frequently in the range of 2 to 12 ueq/L with a pH close to 5.3.

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INTRODUCTION

In recent years research on the atmospheric chemistry of remote areas has increased. This work has led to the identification of important natural sources of acidic and basic emissions and to a better understanding of the transformation, transport, and deposition of sulfate from the remote atmosphere. It is useful to determine typical values for precipitation chemistry from marine air masses approaching the west coast of the United States and Canada to establish a reference point for comparison with urban and industrial areas.

Background concentrations are most commonly measured at sites remote from anthropogenic sources, although sites at great distances may not represent a useful background for some distant region. It is necessary to define carefully the meaning of background relative to the region of interest 1*. While marine background and continental background sites may be influenced by different mixes of chemical compounds 2*, sulfate is nearly always an important or dominant component such that marine background sulfate concentrations are useful for comparison with more polluted areas. Data sets from sites monitored for multiple years are considered appropriate because averaging over time and space helps reduce variability associated with meteorology and sources, respectively.

To separate natural and anthropogenic sources, one of the following definitions of "background" concentration might be appropriate:

1. The lowest concentrations of pollutants observed in the northern hemisphere.
2. The average concentrations that would occur if natural emissions were distributed uniformly over the northern hemisphere.
3. The average concentrations expected if anthropogenic sources did not exist.

Any definition of background must be qualified not only with regard to location but also to meteorology. For example, at a clean site such as the Mauna Loa observatory in Hawaii (at 3400 m elevation), the study of carbon dioxide and aerosol data indicates three different background regimes, one observable during upslope winds and the other two observed with downslope winds 3*. At low-elevation sites along the west coast of North America, a similar difference has been observed in onshore marine air masses and offshore moving continental air masses 4,5*.

The elevation of the Mauna Loa site points out several important aspects of defining background from remote site measurements. The acid-base species available in pre-cloud air, precipitation amount, and scavenging efficiency must be considered when high-elevation samples are considered for use in defining a background. Thus, measurements made at a nearby remote site that is at a much higher elevation or where the precipitation is dominated by snowfall would not be appropriate for estimation of background in lower elevation regions.

A recent review of global background aerosol and precipitation chemistry suggested that remote locations in the Northern Hemisphere had higher sulfate concentrations than the Southern Hemisphere 6*. However, the west coast of North America has very clean precipitation relative to the rest of the continent 7,8,9,10*, and it is cleaner than the Northern Hemisphere background concentrations presented by Schwartz 6*. This is supported by event sampling 11,12* on the coast of Washington state which suggests that rain associated with onshore air flow is similar to rain falling at low altitudes in other remote, mid-latitude marine settings, including southern hemisphere sites 13,14,15,16,17,18,19,20,21*.

If low trace metal concentrations such as Pb, Cd, Cu, Zn, and As are used as the criteria, the cleanest precipitation on the earth falls in Antarctica, the South Pacific Ocean, and Greenland 22,23,24*. Precipitation along the west coast of North America has low concentrations (< 1 ppb) of trace metals 12,25,26,27,28,29*.

A summary of the chemical composition of rainwater measured at remote sites is given in Table I. At remote marine sites, the dominant anion in precipitation should be sulfate 30*. Methane sulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$ or MSA) has been detected in marine precipitation and may be an indicator of marine origin of the sulfate species 31,32*. At remote continental sites, organic acids can be important components of the total anion concentrations 2* especially formate and acetate 33,34*. The important cations are H^+ and NH_4^+ . If these data are representative, they suggest a preliminary estimate of background SO_4^{2-} concentration of about 5 ueq/L, NO_3^- of 3 ueq/L, formate of 1 ueq/L, and ammonium of 2 ueq/L, resulting in a pH close to 5.

Table I: Chemical composition of rainwater collected at remote sites [ueq/L].

Site:	Lake Ozette WA	Amsterdam Island	Poker Flat Alaska	Katherine Australia	Enewetok Atoll
Reference#	a	b	c	d,f	e
H+	5.2	8.8	11.0	16.6	-
SO ₄ =	15.2	29.2	7.2	6.3	-
SO ₄ (xs)=	5.8	4.9	7.1	5.5	5.8
Na+	78.8	206.5	1.0	7.0	48.
Cl-	98.2	237.7	2.6	11.8	57.
Br	-	-	-	-	0.1
Mg++	18.3	45.9	0.2	2.0	14.
NO ₃ -	2.5	1.3	1.9	4.3	-
NH ₄ +	2.3	1.8	1.1	2.0	-
K+	3.0	4.4	0.6	0.9	1.
Ca++	3.8	8.6	0.1	2.5	2.5
RCOOH	0.97	2.2		0.6-53.0	-
MSA	0.07	-	-	-	-
Ratio##:NH ₄ +					
/SO ₄ (xs)=	0.4	0.4	0.2	0.4	-

#Reference: a: Vong et al. 11,12*
b-d: Galloway 13,35*
Galloway and Gaudry 36*
e: Arimoto et al. 37*
f: Keene et al. 33,34*
##Ratio as [ueq/L / ueq/L]

Most of the measurements made in remote locations are either in the southern hemisphere or are of such short duration that their representativeness is uncertain. A reference point from northern hemisphere, mid-latitude precipitation chemistry data is needed for comparison to U.S. and Canadian values for urban and industrial areas. Thus, we analyzed data collected at coastal sites in British Columbia, Washington State, and Oregon to define a background value of rainwater sulfate concentration for the west coast of North America. Before performing this data analysis, we evaluate factors controlling the chemistry of precipitation in remote, marine locations: natural sources and scavenging of gases and aerosol by clouds and precipitation. Within this context a background definition can be provided that will be a useful reference point for evaluating an ecosystem departure from the conditions associated with remote areas with similar characteristics.

Physics and Chemistry of Remote Precipitation

The acidity of precipitation is determined dynamically by a titration of the acidic (e.g., CO₂, SO₂, H₂SO₄, HNO₃, HCOOH) by basic (e.g., NH₃ and CaCO₃), forming materials in air and in atmospheric liquid water. Thus, "background" sulfate concentration cannot be described only by the pH in the absence of local or anthropogenic sulfate; it must also include information regarding ammonia and other important acid-base species 39*.

Sulfate in the cloud water solution, for example, will increase in proportion to the sulfuric acid (H_2SO_4) added to the system, but the presence of basic materials, such as ammonia, means that the H^+ will not increase in proportion to the amount of H_2SO_4 added 40*. This inherent non-linearity between H^+ and SO_4^{2-} in weakly buffered rainwater means that pH is not, by itself, sufficient to characterize the acid-base chemistry of precipitation.

Ultimately, the H^+ availability in precipitation is determined by the emissions of acids and bases into the air mass, production of acids in the air or clouds, transfer of preexisting acidic and basic aerosol and gaseous species into the cloud water, and oxidation of aqueous organic acids to CO_2 .

The primary acid-base components influencing precipitation chemistry in marine air masses moving onshore in remote locations are sulfuric acid, nitric acid, formic acid, methanesulfonic acid, ammonia, calcium carbonate, and, with a small effect, sea salt 35*.

One important source of rainwater solute in marine air is seawater droplets 17,18*, which are produced when air bubbles burst at the sea surface. When these droplets evaporate, aerosol particles are formed. The sea salt contains many species besides sodium and chloride in a sufficiently constant composition so that the fraction of those species attributable to sea salt usually can be subtracted from the measured values. Thus sulfate and calcium often are expressed as "excess" (i.e., the amount not associated with sea salt) 6,18*.

The primary source of sulfuric acid in remote marine air is expected to be the oxidation of $(\text{CH}_3)_2\text{S}$ (dimethylsulfide or DMS), with sulfur dioxide (SO_2) as an intermediate compound. DMS is excreted by certain marine phytoplankton 38*.

The precursors of most acid-base species in precipitation are introduced into the atmosphere as gases. They are removed from the atmosphere by dissolution in atmospheric water (cloud-water or rain), absorption directly at the earth's (or ocean) surface, or by oxidation and physical transformation to aerosol or cloud particles. Particles created by gas-to-particle conversion generally will be less than 1 μm in diameter and will remain airborne with a potential lifetime of about two days 41,42*. Northern hemisphere background sulfate aerosol concentrations are frequently about 0.2 to 0.5 $\mu\text{g}/\text{m}^3$ 6*.

Although gas-phase emission and conversion may be an important consideration in agricultural or industrialized areas, it is expected that along the west coast of North America the concentrations of background gases will be small 43*. Preexisting aerosol and the atmospheric liquid water content should be enough to approximate the acid-base character of the cloud and rain water 30*.

Solid phase precipitation forms by vapor deposition onto ice nuclei, which generally are not soluble. The snow crystal thus may contain very little sulfate. Solid-phase precipitation and rain that is melted snow potentially are chemically different and more dilute than rain 44*; elevation may have a large effect on the composition of precipitation. As elevation increases, temperature decreases, and precipitation formation increasingly involves snow-flake growth by vapor deposition. This results in a decrease in the concentration of the solutes compared to scavenging by liquid phase hydrometeors 44*.

METHODS

Data for the west coast of North America were obtained from the Atmospheric Environment Service of Canada and the U.S. Acid Deposition System (ADS). Data for five sites in British Columbia, Washington, and Oregon were screened for internal consistency and evidence of anthropogenic or terrestrial influences. Histograms of the sulfate data (with and without screening and seasalt corrections) were used to compare sites and define background concentrations.

Other stations were not used in this study because the site locations were judged less likely to produce results that could be described as background. For example, the site in Denali National Park, Alaska, was not included because of possible influences from Anchorage area emissions and its inland, high-elevation location. Coastal sites in California also display higher concentrations of $\text{SO}_4=$, NO_3^- , NH_4^+ , Ca^{++} , and H^+ 45*, presumably due to influences from anthropogenic emission sources. Polluted air transported to the west off the California coast could influence marine sites during subsequent onshore flow.

Data selection

Precipitation chemistry data from sites in the Canadian Network for Sampling Precipitation (CANSAP), the U.S. National Atmospheric Deposition Program (NADP), and the British Columbia Ministry of Environment 46* were examined for their usefulness in this analysis. After a preliminary review, only long-term data from five sites, three in the USA and two in Canada, were used in this study.

The results for the following coastal sites located at Port Hardy and Terrace, British Columbia (1980-83), Alsea Guard Station (1980-85) and Schmidt Farm (1980-83), Oregon, and Hoh River, Washington (1980-85), were used. Their specific locations are as follows:

Hoh River, also called Olympic National Park, in northwestern Washington, latitude $47^\circ 52' \text{N}$, longitude $123^\circ 55' \text{W}$, NADP network.

Alsea, in Suislaw National Forest, NW of Eugene, Oregon, latitude $44^\circ 23' \text{N}$, longitude $123^\circ 37' \text{W}$, NADP network.

Schmidt Farm, also called Hyslop, near Albany, Oregon, latitude $44^\circ 38' \text{N}$, longitude $123^\circ 13' \text{W}$, NADP network.

Port Hardy, on Vancouver Island, Canada, latitude $50^{\circ} 28'N$, longitude $127^{\circ} 22'W$, CANSAP network.

Terrace, in Northwestern British Columbia, latitude $54^{\circ} 28'N$, longitude $128^{\circ} 35'W$, B.C. Ministry of Environmental network.

The sampling records for these five sites were examined and found to be without serious gaps, and analytical procedures were determined to be constant throughout the period of interest. The analytical errors in $SO_4^{=}$, NO_3^{-} , Ca^{++} , NH_4^{+} , and H^{+} are believed to be small enough to allow a precise and accurate evaluation of background values in the concentration ranges presented in Tables I and IV 47,48*. The H^{+} concentrations for these sites likely represent a minimum value (maximum pH) because unpreserved precipitation samples are subject to biodegradation 33,34,49*. Vong 32* collected rainwater on the Washington coast and found increases of about 0.1 pH unit for unpreserved rainwater samples compared to samples that had been refrigerated and chloroformed.

Data Screening

A series of screening tests were applied to the data to eliminate samples that might not be valid or representative of background conditions. As a preliminary step, samples were eliminated when the field-site operator reported obvious problems with the sample's quality or the sample was recorded as snow. The screening was designed to be conservative in the sense that a sample would be rejected only if it was clearly unsuitable. Three subsets of data were formed: a "minimally screened" set where only screening steps one and two (see below) were applied to ensure sample integrity, a second set where sea salt corrections were applied to the sulfate concentrations of samples in the "minimally screened" data set, and third a "fully screened" set where samples with suspected continental or anthropogenic influence were eliminated and seasalt corrections were applied to the sulfate and calcium data.

In the first screening step, a charge balance was calculated as the absolute value of the difference between anions (Cl^{-} , NO_3^{-} , $SO_4^{=}$) and cations (Na^{+} , Mg^{++} , K^{+} , Ca^{++} , NH_4^{+} , H^{+}) divided by the sum of anions and cations. To pass this screening step, a sample was required to have less than a 40% charge balance error; this resulted in samples surviving the entire four-step screening procedure with a mean charge balance error of 7% (about 5 ueq/L).

In the second screening step, sampling efficiency (comparison of rain gauge depth with sample volume) and sea salt (Cl^{-}/Na^{+}) ratios were utilized to identify additional samples of questionable integrity. At marine sites it is important to correctly evaluate sodium concentration if sulfate correction for sea salt is applied to determine "excess sulfate". Rainwater collected within several hundred kilometers of the ocean generally has the same Cl^{-}/Na^{+} ratio as bulk seawater 18,32,45,50*. "Excess (or non-sea-salt) sulfate" concentrations are determined by calculating the concentration of sulfate that would have occurred if all

the sodium in the sample were derived from sea salt, and then subtracting that amount from (analytical) "total sulfate" concentration. The correction is applied by subtracting 0.117 ueq/L [SO_4] for every ueq/L [Na^+] in the sample. "Excess sulfate" and total sulfate are compared in Figure 2.

Poor sampling efficiency (rain collected by the sampler compared to rain collected by a rain gauge) could indicate problems with the sampler operation. A factor of two deviation in sampler efficiency was allowed; data used in the analysis had an efficiency greater than 50% or less than 200%. A sample also was required to be within a factor of two of the expected Cl^-/Na^+ ratio (1.8 by mass, 18,51*. Screening based on the Cl^-/Na^+ ratio was not performed if the Na^+ concentration was relatively small ($\text{Na}^+ < 40$ ueq/L), because the sea salt correction for sulfate would be small. Screening steps 1 and 2 constitute checks for sample integrity.

Few sampling sites at mid-latitude locations in North America are always isolated from anthropogenic emissions sources; aerosol concentrations were much lower along the coast of Washington during onshore flow than when air trajectories had passed over continental areas 4*. Precipitation concentrations at Bermuda vary considerably depending upon air trajectory 52*. Rain along the west coast generally occurs under southwest flow from the Pacific 53*; most precipitation samples would be collected during onshore flow 11*. It would be desirable to identify rain samples collected during offshore flow or during onshore flow with a past overland trajectory. A meteorological analysis cannot provide this information because of the weekly and monthly sampling intervals. Later we present a principal component analysis of the "minimally screened" rainwater data to indicate that continental and anthropogenic sources are still influencing some samples in that data subset.

Screening steps 3 and 4 identify samples with evidence of a period of continental residence for the air mass. Studies of precipitation chemistry in very isolated locations 13,36* or that selected 'clean' air trajectories 11,12,32,39* suggested upper limits for three components of background precipitation: nitrate, ammonia, and calcium (all indicative of terrestrial emission sources). These criteria were derived from northern hemisphere sampling 11*, but they are consistent with southern hemisphere data 13,14*.

Application of screening step 3 to the data from the west coast of North America asks: what are the sulfate concentrations in rainwater samples that have nitrate concentrations (an 'anthropogenic tracer') in the same range as that of clean rainwater collected elsewhere? The levels for screening are defined from Vong et al. 11,12*, Quinn et al. 39* (samples always contained less than 5 ueq/L each of nitrate and ammonium ion), Galloway and Gaudry 36* and Galloway et al. 14* (NO_3^- concentrations were less than 5 ueq/L, 95% confidence; NH_4^+ was less than 5 ueq/L).

Calcium, especially as calcium carbonate, is a major earth mineral and may be evidence of contamination by wind-blown dust. However, calcium is also a significant component of seawater. Therefore, "excess calcium" (Caxs) is calculated to remove the seasalt contribution ($\text{Ca}^{++} - 0.0378 * \text{Na}^+$ for mg/L units). In screening step 4, rainwater samples with NH_4^+ greater than 5 ueq/L (see above) or with more than 10 ueq/L Caxs++ were removed from the data. Most remote rainwater samples have excess calcium less than 10 ueq/L 13*. This definition for background sulfate concentration is based on an indirect indicator of marine air trajectories, that is, samples with Caxs++, NO_3^- and NH_4^+ concentrations less than screening levels derived from experiments in which only 'clean air' was sampled.

RESULTS

The effect of the screening procedure was investigated by tracking the number of samples surviving each of the four screening steps. Sulfate concentrations were compared with and without the final two steps of screening and with and without the correction for seasalt sulfate. Mean concentrations for five species key to the acid-base chemistry are presented as well as a multivariate analysis used to identify correlations between the variables in the "minimally screened" data.

Effects of Screening

A total of 385 rainwater samples survived the four-step screening procedure, which represented 62% of the 617 rain samples chemically analyzed by the NADP and CANSAP laboratories for these five sites. As seen in Table II, the largest number of samples were eliminated due to the sea-salt-sampler efficiency ratios at the Hoh (30 samples eliminated / 219 total samples), Terrace (15/46), and Schmidt (39/125) sites. At the Alsea (31/180) and Schmidt (37/125) sites, a number of samples were dropped due to nitrate concentration but at Pt.Hardy the greatest number of samples (7/47) were dropped due to the NH_4^+ and Ca^{++} screening step. For most sites relatively few samples were eliminated due to the last screening step (excess calcium or ammonium). Overall, 15% of the samples were eliminated due to nitrate screening but only 6% were eliminated at the northern three sites (British Columbia, Vancouver Island, and Washington).

Table II. Number of samples remaining after each step of the screening.

Site	Alsea	Schmidt	Hoh	Pt.Hardy	Terrace
Dates:	1980-85	1980-83	1980-85	1980-83	1980-84
N	180	125	219	47	46
N1	177	122	212	46	45

N2	164	83	182	42	30
N3	133	46	167	38	30
N4	128	35	162	31	29

Number of samples surviving four successive screening steps:

N = Number of rain samples chemically analyzed by the network.

N1 = Number within 40% of charge balance (passed step 1).

N2 = Number with sea-salt ratio and sampler efficiency between 50-200% (passed step 2).

N3 = Number with $\text{NO}_3^- < 5 \text{ ueq/L}$ (passed step 3).

N4 = Number with both $\text{Caxs}^{++} < 10 \text{ ueq/L}$ and $\text{NH}_4^+ < 5 \text{ ueq/L}$ (passed step 4).

Estimates of Background

For purposes of this paper, background sulfate concentration in rainwater was defined as a range of values observed in weekly or monthly samples collected at the most remote, low elevation sites on the west coast of North America (after eliminating sea salt contributions). The measurement sites selected for analysis were upwind of population and industrial centers, and it was possible to identify, and exclude, individual measurements that appeared to be influenced by anthropogenic sources. For reasons stated earlier, this definition also excludes measurements taken during precipitation in the form of snow. Five sites that met the above criteria, two in British Columbia, Canada, one in Washington, and two in Oregon were selected for analysis. There is no a priori reason to believe that these sites are different with respect to observed background sulfate values.

Following selection of these sites, the aqueous concentration of sulfate in rainwater, rather than the deposition rate of sulfate via rain, was selected as the appropriate variable. This decision was based partly on the fact that the concentration of sulfate does not display a significant correlation with weekly precipitation amount at these marine sites. The total amount of rain in a year varies among the five coastal sites and varies considerably between the coast and any inland region of interest (as much as a factor of three). It is rainwater sulfate concentration rather than sulfate wet deposition that is a common characteristic of these five coastal sites. The removal of sulfate species from the air is a relatively inefficient mechanism; a correspondingly large atmospheric residual amount of sulfur is not removed in any given rain event over spatial scales of 100 km 54^* . Therefore, if deposition were chosen, geographic variability in the amount of rain between the background reference point and any inland regions becomes the single most important determinant of any comparison of sulfate deposition rate. The choice of sulfate concentration in rainwater, rather than deposition rate, eliminates this potential rainfall bias.

Based on the above approach, the sulfate concentration measurements at the five sites were screened to require internal consistencies of sample volume to rain gauge measurements, ionic balance, and a sodium-to-chloride ratio similar to seawater. Histograms of the "fully screened and minimally screened" data for one site are presented in Figure 2. The Schmidt, OR, site is presented to illustrate the effect of screening on the data for the site that had the largest fraction of samples fail screening step 3. The location of the Schmidt, OR, site is further inland than the other sites analyzed here; more frequent continental influence (see Table II) is not surprising. Histograms for the other four sites are presented elsewhere 47*.

A principal component analysis of the "minimally screened" data for the five sites demonstrated that seasalt was the predominant source of chemical variability (see Table III). Therefore, the sulfate correction using sodium ion concentration as an index of sea salt was necessary to remove sea salt contributions to total sulfate. Additional sources were weakly indicated, with the suggestion of a soil-derived or combustion factor (PC#2). Unfortunately, no tracers of marine excess sulfate (such as MSA) were available for this analysis.

 Note to Page Craft, please be aware of lining up the information under PC#1, one set of Na, Cl, Mg for each site except Terrace is only Na Cl *****

Table III: Principal component analysis of the "minimally screened" data (i.e.- after screening steps 1 and 2):

Site:	Alsea	Schmidt	Hoh	Pt. Hardy	Terrace
All Sites					
PC#1					
Na+,Cl-,Mg++	Na+,Cl-,Mg++	Na+,Cl-,Mg++	Na+,Cl-,Mg++	Na+,Cl-,Mg++	Na+,Cl-
Na+,Cl-,Mg++					
PC#2	Caxs++	Caxs++	H+	NH ₄ +	Caxs++
H+					
SO ₄ xS=	SO ₄ xS=	H+	SO ₄ xS=	NO ₃ -	Mg++
SO ₄ xS=			NO ₃ -		
Caxs++					

SO₄xS= and Caxs++ have been corrected for sea salt, see text.

Figure 2 shows the original total sulfate histograms (solid) for the Schmidt site and the "excess sulfate" histograms (cross-hatched) resulting from this correction. A substantial number of the high sulfate observations (20 ueq/L) were associated with high seasalt levels. Because the sea salt sulfate is largely contained in large aerosol (dia. > 1 μ m), this portion of the background aerosol would be quickly removed as an air mass moves inland and is not useful as a reference point for inland areas. Histograms for the other sites were similar 47*.

The sea salt correction alone is not adequate for the analysis of background sulfate concentrations. It is required that no known anthropogenic sources should influence the measurements. To this end, the screening criteria described as steps 3 and 4 were established based on source information gained from principal component analysis (Table III, PC#2) and knowledge of precipitation chemistry for event samples at remote locations. The nitrate and ammonium ion restriction was based on the ocean not being a significant source of these ions, whereas the excess calcium screening criteria reduced the influence of crustal material.

Figure 2 shows the excess sulfate frequency distribution after this final screening procedure as the "fully screened" value. The high values (>20 ueq/L) in the minimally screened data (steps 1 and 2) are virtually eliminated from the fully screened data. Shifts in the distributions for the other four sites also occurred with seasalt corrections and full screening.

These distributions provide the concentration values expected for "background" sulfate from weekly to monthly sampling intervals. The distributions reflect the influence of a widely distributed, sub-micrometer sulfate aerosol and its influence on coastal, lowland rainwater 11,30,55*. Using the Junge equation, 18* with fine sulfate aerosol concentrations of 0.2 to 0.4 μ g/m³ appropriate for remote areas 6*, nucleation scavenging efficiencies of 0.8 to 1.0 11,56*, and cloud liquid water contents of 0.5 to 1.0 g/m³ 11,30,57,58*, one would expect background rainwater sulfate concentrations to vary between 3 and 16 ueq/L. This aerosol is expected to influence rainwater chemistry in a similar way at these sites as it does at the downwind region of interest, absent the effects of altitude mentioned above.

Support for this notion of a widely distributed sulfate aerosol is noted when one compares the excess sulfate distributions for rainwater at each of the five sites with the average distribution for all five sites; their similarity suggests a general widespread background concentration that is relatively invariant over space along the west coast of North America when multi-annual averaging periods are considered. This finding is consistent with the widespread distribution of the likely emission source: production of DMS by biological activity in upwelling areas of the ocean and over the open ocean 35,38*.

Figure 3 presents two versions of the frequency distribution of "fully screened excess" sulfate for all five sites [the data were summarized both by weighting each site equally (solid) or by weighting by the number of samples collected (cross-hatched)]. The two presentations are very similar, with about 86% of the samples having excess sulfate between 2 and 12 ueq/L and a few samples with concentrations between 14 and 22 ueq/L. This results in mean or median values lower than Schwartz's 6* estimate of a mean background precipitation sulfate concentration of 10-15 ueq/L for the Northern Hemisphere. The data analyzed here are entirely consistent with Schwartz's background sulfate aerosol data and nucleation scavenging theory, which predicts 3-16 ueq/L background sulfate for rain. Schwartz's rainwater data were primarily from Bermuda and the Arctic but his aerosol data covered a much larger portion of the Northern Hemisphere. Clearly, the Pacific Coast of Washington, Oregon, and British Columbia experiences very clean rain.

The sulfate ion concentrations shown in Figure 3 are the best estimate of the background sulfate in rainwater on the west coast of North America. A distribution is more appropriate than a single value because the background is expected to vary over time with variation in emission sources and meteorology. It is emphasized that this distribution is applicable over an annual averaging period with a one-week to one-month sampling time.

Table IV presents the chemical composition for the "fully screened" data set (i.e., after screening steps 1-4). Neglecting seasalt, sulfate is the dominant anion in rainwater while hydrogen ion (mean= 5 ueq/L) is usually the most important cation for these samples. Nitrate (mean= 1 ueq/L) is present at levels less than 50% of excess sulfate concentration. Ammonium was always very low (< 2 ueq/L) at these coastal sites. No data were available for organic anions. These results are consistent with our preliminary estimate of 5 ueq/L for excess sulfate in background rainwater. The mean pH of 5.3 is slightly higher than the value of 5.0 predicted from event sampling, possibly because of slightly higher levels of cations such as Caxs (mean= 2 ueq/L), especially at the Alsea and Terrace sites. The weekly/monthly sampling intervals underestimate H⁺ because of biodegradation of organic acids; the 'true' pH for these sites would be below 5.3 (see above).

Table IV: Precipitation composition for five sites along the west coast of North America ("fully screened data", i.e., after screening steps 1-4) [ueq/L] (volume-weighted mean).

Site	Alsea OR	Schmidt OR	Hoh WA	Pt.Hardy B.C.	Terrace B.C.	All Five ^a
Rainfall [mm/wk]	48.3	44.1	73.2	46.7	28.5	48.1
Charge Bal	0.05	0.08	0.07	0.07	0.19	0.07
Cl-/Na+	1.8	2.2	2.5	1.7	2.1	2.1

N	128	35	162	31	29	385
Na+	45.0	13.0	24.0	66.0	5.4	34.0
SO ₄ xs=	5.5	5.0	4.4	6.4	7.8	5.5
NO ₃ -	1.7	2.5	1.4	1.4	0.6	1.4
H+	3.6	3.2	3.7	8.3	7.5	5.1
NH ₄ +	1.4	2.0	1.4	0.7	0.4	1.2
Ca _{xs} ++	3.8	2.0	1.3	3.4	4.1	2.2

a All= precipitation-weighted mean of all samples for the five sites.

It is interesting to note the fairly large differences in weekly precipitation amount (mean/range = 1) between the five sites in contrast to the relatively consistent values for rainwater sulfate concentrations (mean/range= 0.6). The wet deposition of excess sulfate is directly related to precipitation amount in background locations but is relatively independent of sulfate concentration. This is consistent with the concept of concentration rather than deposition as the most representative characteristic of background rainwater composition along the west coast of North America.

The sulfate concentrations reported here are useful as an estimate of background along the west coast of North America as a reference point with which to compare data from industrial and urban areas. Sulfate should be a more useful characteristic of background than pH because excess sulfate is a conservative tracer whereas H⁺ is easily removed from the system by addition of bases such as soil dust or ammonia. A comparison of background with industrial/urban precipitation composition was conducted by Galloway et al. 14* using remote data that was collected mostly in the Southern Hemisphere or distant from continental land masses. Our analysis indicates that their comparison holds true when mid-latitude, Northern Hemisphere precipitation composition is used as the reference value.

It is not known at this time how far inland the air masses are influenced by the marine sulfate aerosol; given a lifetime of about two days for sub-micrometer sulfate aerosol, this background concentration would be expected to persist on the order of a few hundred kilometers. Naturally occurring terrestrial emissions could add to marine excess sulfate, and scavenging processes could alter the incoming marine air before reaching urban/industrial areas. Therefore, it is important to distinguish this reference value (2-12 ueq/L excess sulfate) from the actual contribution of the marine aerosol farther inland or the sum of all natural contributions, both of which are unknown at this time.

CONCLUSIONS

The description of the acid-base chemistry of precipitation and mechanisms of precipitation formation imply that any useful interpretation of precipitation measurements must consider those

perspectives. Data derived from rain must be separated from data derived from snow measurements. For the purposes of this report, "background" sulfate was defined as the range of concentration in weekly or monthly samples of rain collected over multi-annual periods at remote sites, upwind of urbanized areas, with the further requirement that data with evidence of possible anthropogenic source contamination be excluded.

In the marine air masses studied in this report, sulfate was the dominant ion in the acid-base balance; other ions were present but were less important in a charge balance sense. The screening techniques appear to have been successful in defining a useful reference value for excess sulfate whose spatial consistency reflects a widespread sulfate aerosol oceanic source and whose temporal variation is consistent with the concept of nucleation scavenging of that sulfate aerosol by liquid water. Since this background sulfate is only slowly removed by rainfall, the region of non-sea-salt, marine sulfate influence may extend approximately several hundred kilometers downwind from the west coast of North America.

Values obtained from several long-term record sites along the west coast of North America were mutually consistent and suggest a background excess sulfate concentration in the range of 2 to 12 ueq/L for most weekly and monthly samples. The distribution has a mode of approximately 8 ueq/L with a mean of 5.5 ueq/L for 3 to 5 years data at each of five sites. The average measured pH of this rainwater was 5.3, but actual pH values are likely to be slightly lower than the measured values due to changes in sample composition between collection and chemical analysis.

REFERENCES

- 1 Summers, P.W., "Regional Background Atmospheric Sulphate Levels in Canada: Preliminary Estimates and Implications for Control Strategies", Atmos. Environ. Service of Canada Report, Downsview, ONT (1985).
- 2 Keene, W.N. and Galloway, J.N., "The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding", Tellus 40B, 322-34 (1988).
- 3 Shaw, G.E. "Transport of Asian Desert aerosols to the Hawaiian Islands", J. Applied Met. 19, 1254-59 (1980).
- 4 Fox, T.D. and Ludwick, J.D., "Lead concentrations associated with 1000 mb back trajectories at Quillayute, Washington", Atmos. Environ. 10: 799-803 (1976).
- 5 Ludwick, J.D., Fox, T.D., and Garcia, S.R., "Elemental concentrations of northern hemispheric air at Quillayute, Washington", Atmos. Environ. 11, 1083-7 (1978).
- 6 Schwartz, S.E., "Are global cloud albedo and climate controlled by marine phytoplankton?", Nature 336: 441 (1988).

- 7 Vong,R.J. and Larson,T.V. , "A Critical Review of Acid Deposition Research in the Pacific Northwest", Seattle,WA: Puget Power and Light Co. Research Project 1983-1, Final Report (1983).
- 8 Nikleva,S. (1983), Acid Rain on the West Coast of British Columbia (Vancouver,B.C.: Atmospheric Environment Service), Report 8305-4 PAES
- 9 Vong,R.J., Larson,T.V., Covert,D.S. and Waggoner,A.P., "Measurement and modeling of Western Washington precipitation chemistry", Water, Air and Soil Pollution, 26: 71-84 (1985b).
- 10 Powers,C.F. and Rambo,D.L., "A review of precipitation chemistry in the western USA", Environ. Monitor. Assess., 1: 93-105 (1981).
- 11 Vong,R.J., Hansson,H.-C., Covert,D.S., and Charlson,R.J., "Acid rain: simultaneous observations of a natural marine background and its acidic aerosol precursor", Geophys. Res. Lett. 14, 4: 338-341 (1988a).
- 12 Vong,R.J., Hansson,H.-C., Ross,H.B., Covert,D.S., and Charlson,R.J., "Northeastern Pacific submicrometer aerosol and rain-water composition: a multivariate analysis", J. Geophys.Res. 93, D2: 1625-37 (1988b).
- 13 Galloway,J.N., Likens,G.E., Keene,W.C., and Miller,J.M. , "The Composition of Precipitation in Remote Areas of the World", J. Geophys. Res. 87: 8871-8886 (1982a).
- 14 Galloway,J.N., Likens,G.E., and Hawley,M.E., "Acid precipitation: natural versus anthropogenic components", Science 226: 829-31 (1984).
- 15 Eriksson,E., "The chemical composition of Hawaiian rain", Tellus 9: 509-20 (1957).
- 16 Junge,C.E., "The concentration of nitrate and ammonium in rain water over the United States", Trans. Amer. Geophys. Union, 39: 241-8 (1958a).
- 17 Junge,C.E. and Werby,R.T., "The concentration of chloride, sodium, potassium, calcium, and sulfate in rain water over the United States", J. Meteorology, 15: 417-25 (1958b).
- 18 Junge,C.E., Air Chemistry and Radioactivity, New York: Academic Press (1963).
- 19 Dayan,U., Miller,J.M., Keene,W.C., and Galloway,J.N. , Atmos. Environ. 19: 651-657 (1985).
- 20 Likens,G.E., Keene,W.C., Miller,J.M., and Galloway,J.N., J. Geophys.Res. 92: 13299 (1987).
- 21 Miller,J.M. and Yoshinaga,A.M., "The pH of Hawaiian precipitation, a preliminary report", Geophys. Res. Lett. 8: 779-82 (1981).
- 22 Legrand,M.R. and Delmas,J.R., "The ionic balance of Antarctic snow: a 10-year detailed record", Atmos. Environ. 18, 9: 1867-74 (1984).

- 23 Galloway, J.N., Thornton, J.D., Norton, S.A., Volchok, H.L., and McLean, R.A.N., "Trace metals in precipitation, a review and assessment", *Atmos. Environ.* 16: 1677-1700 (1982b).
- 24 Davidson, C.I., Goold, W.D., Mathison, T.P., Wiersma, G.B., Brown, K.W., and Reilly, M.T., "Airborne trace elements in Great Smoky Mtn, Olympic, and Glacier National Parks", *Environ. Sci. Tech.* 19: 27-35 (1985).
- 25 Rancitelli, L.A. and Perkins, R.W., *J. Geophys. Res.* 75: 3055-64 (1970).
- 26 Tanner, T.M., Rancitelli, L.A. and Haller, W.A., "Water, Air, and Soil Poll.", 1: 132-43 (1971).
- 27 McLaren, R.R., "Lower Mainland and South Coast B.C. Precipitation Chemistry Data", Vancouver, B.C.: Atmospheric Environment Service Pacific Region, Report PAES 85-2 (1985).
- 28 McLaren, R.R., "Lower Mainland Precipitation Chemistry Data", Vancouver, B.C.: Atmospheric Environment Service Pacific Region, Report PAES 82-4 (1982a).
- 29 McLaren, R.R., "Sampling of Snowpacks for Chemical Analysis in Southwestern British Columbia", Vancouver, B.C.: Atmospheric Environment Service Pacific Region, Report PAES 82-3 (1982b).
- 30 Charlson, R.J. and Rodhe, H., "Factors controlling the acidity of natural rainwater", *Nature* 295: 683-5 (1982).
- 31 Saltzman, E.S., Savoie, D.L., Zika, R.G. and Prospero, J.M., *J. Geophys. Res.* 88, C15, 10897 (1983).
- 32 Vong, R.J., "Simultaneous Observations of Rainwater and Aerosol Chemistry at a Remote Mid-Latitude Site", PhD Dissertation, University of Washington, Seattle, WA. (1985).
- 33 Keene, W.C., Galloway, J.N., and Holden, J.D., "Measurement of Weak Organic Acidity in Precipitation from Remote Areas of the World", *J. Geophys. Res.*, 88: 5122-30 (1983a).
- 34 Keene, W.C., Galloway, R.J., and Holden, J.D., "Organic Acidity in Precipitation for Remote Areas of the World", *Proc. 3rd Nat. Sympos. on Recent Advances in Measurement of Pollutants in Ambient Air and Stationary Sources*, USEPA, RTP, NC. (1983b).
- 35 Galloway, J.N., in *The Bio-geochemical Cycling of Sulphur and Nitrogen in the Remote Atmosphere: NATO Advanced Research Workshop*, Galloway, J.N., Charlson, R.J., Andreae, M.O., Rodhe, H., (eds.), D. Reidel Publishing Co., Dordrecht (1985).
- 36 Galloway, J.H. and Gaudry, A., "The composition of precipitation on Amsterdam Island, Indian Ocean", *Atmos. Environ.* 18: 2649-56 (1984).
- 37 Arimoto, R., Duce, R.A., Ray, B.J., and Unni, C.K., "Atmospheric trace elements at Enewetok Atoll, 2. Transport to the ocean by wet and dry deposition", *J. Geophys. Res.* 90: 2391, (1985).

- 38 Andreae, M.O. and Raemdonck, H., "Dimethylsulfide in the surface ocean and marine atmosphere: a global perspective", *Science* 221: 744 (1983).
- 39 Quinn, P.K., Charlson, R.J., and Bates, T.S., "Simultaneous observations of ammonia in the atmosphere and ocean", *Nature* 335: 336 (1988).
- 40 Vong, R.J. and Charlson, R.J., "The pH of a cloud or rain drop: a computer based solution for a six component system", *J. Chem. Educ.* 62: 141-3 (1985).
- 41 Pruppacher, H.R. and Klett, J.D., *Microphysics of Clouds and Precipitation*, D. Reidel Publ., Boston (1980).
- 42 Rodhe, H. and Grandell, J., "On the removal time of aerosol particles from the atmosphere by precipitation scavenging", *Tellus* 24, 5: 442 (1972).
- 43 Andreae, M.O., Berresheim, H., Andreae, T.W., Kritz, M.A., Bates, T.S., and Merrill, J.T., "MSA, sulfate, and SO₂ in air over the eastern portion of the North Pacific", *J. Atmos. Chem.* 6: 149 (1988).
- 44 Scott, B.C., "Sulfate Washout in Winter Storms", *J. Applied Met.*, 20, 619-625, (1981).
- 45 Gibson, J.H., "NADP/NTN annual data summary, precipitation chemistry in the United States", Colorado State University, Ft. Collins, CO (1987).
- 46 Sandberg, W., "Precipitation Monitoring Reports for Agassiz, Kitimat, Pender, Sechart, Squamish, Smithers, and Victoria", British Columbia Ministry of the Environment, Victoria, BC, (1985).
- 47 Sagert, P.G., Ruby, M.G., Fane, B., Frazer, J.L., Charlson, R.J., Duncan, L.C., Larson, T.V., and Vong, R.J., "Background Concentrations of Sulphate in Precipitation along the British Columbia Coast", Report PAES-86-1, Atmos. Environ. Service of Canada, Vancouver, B.C. (1986).
- 48 Sisterson, D.L., Wurfel, B.E., and Lesht, B.M., "Chemical Differences Between Event and Weekly Precipitation Samples in Northeastern Illinois", *Atmos. Environ.* 19: 1453 (1985).
- 49 Keene, W.N. and Galloway, J.N., *Atmos. Environ.* 18, 2491, (1984).
- 50 Granat, L. and Soderlund, R., "Atmospheric Deposition Due to Long and Short Distance Sources", University of Stockholm, Dept. of Meteorology, Report AC-32, Stockholm, Sweden (1975).
- 51 Holland, H.D., *The Chemistry of the Atmosphere and Oceans*, New York: John Wiley and Sons, (1978).
- 52 Moody, J.L. and Galloway, J.N., "Quantifying the relationship between atmospheric transport and the chemical composition of precipitation on Bermuda", *Tellus* 40B, 463-79 (1988).

53 Overland, J.E. and Walter, B.A., "Marine weather of the inland waters of western Washington", NOAA report EML-44, Nat. Ocean. and Atmos. Admin., Seattle, WA (1983).

54 Vong, R.J., Moseholm, L., Covert, D.S., Sampson, P., O'Loughlin, J., Stevenson, M., Charlson, R.J., Zoller, W.H., and Larson, T.V., "Changes in rainwater acidity associated with closure of a copper smelter", J. Geophys. Res. 93, D6: 7169-79 (1988c).

55 Savoie, D., "Nitrate and non-sea-salt sulfate aerosols over major ocean regions of the world ocean: concentrations, sources, and fluxes", PhD thesis, University of Miami, Miami, FL (1984).

56 Jensen, J.B., and Charlson, R.J., "On the efficiency of nucleation scavenging", Tellus 36B, 5: 367-75 (1984).

57 Hobbs, P.V. and Persson, P.O.G., "The mesoscale and microscale organization of clouds and precipitation in mid-latitude cyclones, V. The substructure of narrow cold frontal rainbands", J. Atmos. Sci. 39: 295 (1982).

58 Wang, P.Y. and Hobbs, P.V., "The mesoscale and microscale structure and organization of clouds and precipitation in mid-latitude cyclones, X. Wavelike rainbands in occlusion", J. Atmos. Sci. 40: 1959 (1983).

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Figure 1:



FIGURE 2 SCHMIDT OREGON SITE:
TOTAL & EXCESS SULFATE

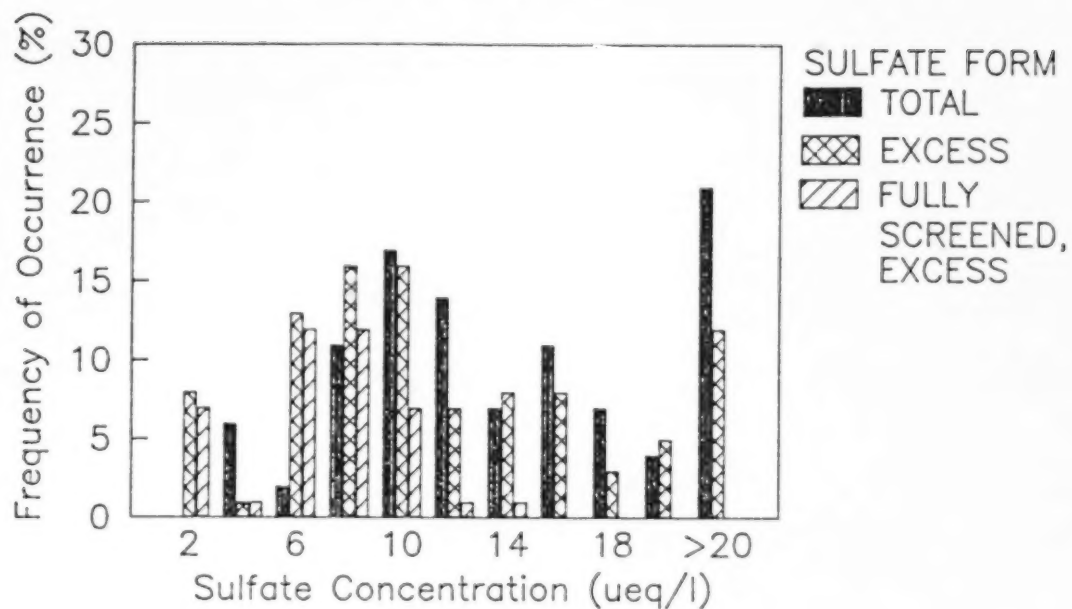


FIGURE 3 EXCESS SULFATE CONCENTRATION
FOR ALL STATIONS

